Investigation of MBE-grown $\text{InAs}_{1-x}\text{Bi}_x$ Alloys and Bi-mediated Type-II Superlattices by Transmission Electron Microscopy

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Abstract:

The microstructure of $\text{InAs}_{1-x}\text{Bi}_x$ ($x \sim 4.5\%$ and $\sim 5.8\%$) films and Bi-mediated $\text{InAs}/\text{InAs}_{1-x}\text{Sb}_x$ type-II superlattices grown by molecular beam epitaxy on GaSb (001) substrates has been investigated by electron microscopy techniques. Lateral compositional modulation exists in both smooth and hazy regions of all InAsBi films observed but no atomic ordering is apparent in current imaging projections. Surface droplets present in hazy regions assume a zincblende crystalline structure that is usually tilted relative to the underlying dilute bismide film. Study of Bi-mediated $\text{InAs}/\text{InAs}_{0.81}\text{Sb}_{0.19}$ type-II superlattices indicates that the InAs-on-InAsSb interface still appears broadened relative to the InAsSb-on-InAs interface.

Keywords: A1. Phase separation, A1. Interface abruptness, A3. Type-II superlattices, A3. Molecular beam epitaxy, B1. Bismides, B3. Infrared detection.

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1. Introduction

III-V-Bi alloys have potential applications in uncooled long-wavelength infrared photo-detectors and lasers due to their large bandgap reduction and relatively temperature-insensitive band gap, and the synthesis of dilute bismides has been actively pursued with different growth techniques to take advantage of such properties [1-4]. Despite the great promise that the dilute bismides hold, the successful growth of such thin films is very challenging and suffers from a large miscibility gap because the alloys are formed through isoelectronic substitution of group-V elements with very different atomic size. Microstructural studies done on epitaxial $\text{GaAs}_{1-x}\text{Bi}_x$ films grown by molecular beam epitaxy (MBE) have shown that the film morphology departs from homogeneity in several ways, including phase separation [5], atomic ordering [5, 6] and surface-droplet formation [7], despite all the efforts directed towards optimizing the growth. In comparison, the growth of $\text{InAs}_{1-x}\text{Bi}_x$ alloys by MBE has only recently been established [8-10], and there is a need for detailed microstructural study of such alloys.

An alternative design for long-wavelength infrared photo-detection is the strain-balanced type-II superlattice (T2SL) system [11], where bandgap engineering can be achieved by varying the superlattice period (layer thickness/composition) and coherent interfacial strain. Recent progress has been made in the design, growth and characterization of Ga-free $\text{InAs}/\text{InAs}_{1-x}\text{Sb}_x$ T2SL with very high structural quality, and the SL interface abruptness seems to play a significant role in affecting the emission properties [12-14]. Growth front coverage with surfactants of at most a few monolayer thickness has been used in MBE to help improve the surface/interface morphology and material properties. For example, Sb was used as a non-reactive surfactant for the growth of AlGaAs , and the surface morphology was improved at all growth temperatures investigated [15]. It continues to be of interest to investigate the effectiveness of surfactants on interface roughness.

In this study, the microstructures of 1- μm $\text{InAs}_{1-x}\text{Bi}_x$ films and bismuth-mediated $\text{InAs}/\text{InAs}_{1-x}\text{Sb}_x$ type-II superlattices grown on GaSb (001) substrates were investigated by transmission electron microscopy (TEM). Incorporation of bismuth into the $\text{InAs}_{1-x}\text{Bi}_x$ films was studied with different imaging techniques, while the emphasis for the T2SL studies was on characterization of the interface abruptness and thus the possible beneficial effect of the Bi surfactant.

2. Experimental Details

All samples were grown on (001) GaSb substrates using a VG-V80H solid source MBE system. The two $\text{InAs}_{1-x}\text{Bi}_x$ samples ($x \sim 4.5\%$ and $\sim 5.8\%$) investigated here were grown at a substrate temperature of 280 °C with different V/III flux ratios. As shown by the schematic in Fig. 1 (a), after growth of the 600-nm-thick GaSb buffer, a 15-nm InAs spacer layer was grown, followed by a 1- μm $\text{InAs}_{1-x}\text{Bi}_x$ film and a 10-nm InAs capping layer. The T2SL sample studied consisted of 56.5 periods of 8-nm $\text{InAs}_{1-x}\text{Sb}_x$ ($x = 19\%$) and 9-nm InAs layers, as indicated in Fig. 1 (b), and was grown at a substrate temperature of 430 °C. The Bi flux (Bi/In flux ratio = 3%) was switched on during growth of the last 40nm of the GaSb buffer layer, and was kept on throughout the growth of the entire superlattice structure as well as the 100-nm GaSb capping layer. Additional growth details are provided elsewhere [10].

TEM samples were prepared for cross-section observation along $\langle 110 \rangle$ -type projections using standard mechanical polishing and dimple grinding, followed by argon-ion-milling (maximum beam energy 2.3 keV) under liquid-nitrogen cooling in order to reduce the ion-beam damage [16]. Electron microscopy was performed using a JEOL JEM-4000EX high-resolution electron microscope with an accelerating voltage of 400 kV and structural resolution of 1.7 Å.

Geometric phase analysis (GPA) to extract information about interfacial strain [17] was applied to the high-resolution electron micrographs using a Digital Micrograph script [18].

3. Results and Discussion

3.1 InAs_{1-x}Bi_x alloys

All surfaces of the InAs_{1-x}Bi_x films had smooth droplet-free regions and hazy droplet-forming regions [10], and measurements using X-ray diffraction (XRD) indicated less Bi incorporation in InAs_{1-x}Bi_x films under the hazy regions. Moreover, broadened X-ray peaks were observed for the droplet-free regions, suggesting non-uniform composition [10]. Reciprocal space maps in the vicinity of the (115) reflection indicate that the InAsBi layers are pseudomorphically strained to the GaSb substrate.

The first sample studied by TEM had a maximum Bi incorporation of 5.8% as measured by (004) ω -2 θ high-resolution XRD scan, assuming a theoretical lattice-constant calculation for InBi. A TEM sample was prepared from the droplet-free region. As indicated by the bright-field image in Fig. 2 (a), very few structural defects were visible over wide lateral distances. Selected-area electron diffraction patterns, as shown by the inset, gave no indication of atomic ordering along this viewing projection. Diffraction-contrast images such as Fig. 2 (b) gave enhanced contrast due to differences in mass/thickness: The vertical stripe features visible in this micrograph thus indicate the occurrence of lateral compositional modulation on the scale of several tens of nanometers.

High-resolution electron micrographs to investigate the interfacial coherence were taken close to the substrate, and near the top, of the InAs_{1-x}Bi_x films, as shown in Figs. 3 (a) and Fig. 4 (a), respectively. These lattice-fringe images showed the excellent crystallinity of the film. The technique of geometric phase analysis can then be used to extract both in-plane and out-of-plane

strain across the epitaxial layers, where the out-of-plane strain (in the $\langle 001 \rangle$ growth direction) due to the tetragonal distortion of the alloy lattice is defined by the expression:

$$\xi_{zz} = \frac{c_{\text{alloy}} - c_{\text{reference}}}{c_{\text{reference}}} \quad (1)$$

In Eqn. (1), c is the lattice parameter along the growth direction.

The in-plane strain (not shown) extracted from both images was negligible, as expected. For the out-of-plane strain analysis of the lattice-fringe image recorded close to the substrate, the unstrained GaSb buffer layer was used as the reference in Eqn. (1). The InAs spacer under tensile strain was readily identifiable in the strain map obtained and in the averaged line profile (averaged perpendicular to the growth direction). Bi started incorporating into the $\text{InAs}_{1-x}\text{Bi}_x$ layer shortly after, if not immediately after, growth of the InAs spacer layer, as evident from the reduced tensile strain in the $\text{InAs}_{1-x}\text{Bi}_x$ layer compared with that in the InAs spacer. Bi incorporation increased the lattice spacing in the $\text{InAs}_{1-x}\text{Bi}_x$ film and thus reduced its lattice mismatch with respect to the unstrained GaSb buffer. However, insufficient Bi was incorporated to achieve exact lattice match so that the $\text{InAs}_{1-x}\text{Bi}_x$ layer remained under slight tensile strain.

Figure 4 (a) shows the excellent crystallinity near the top surface, and the coherent interface between the $\text{InAs}_{1-x}\text{Bi}_x$ film and the InAs capping layer. Again GPA analysis brings out the strain information embedded in high-resolution micrographs and the out-of-plane strain map obtained is shown in Fig. 4 (b). In this case, the InAs capping layer was used as the reference. Thus, the $\text{InAs}_{1-x}\text{Bi}_x$ was under compressive strain as shown by the positive strain value in the averaged line profile (Fig. 4 (c)). A qualitative comparison of the averaged out-of-plane strain in the $\text{InAs}_{1-x}\text{Bi}_x$ film close to the cap in Fig. 4 (c) and close to the substrate (Fig. 4 (d), obtained from further GPA analysis of Fig. 3 (a) but using InAs as the reference) shows that the strain difference of the InAs cap and the top region of the $\text{InAs}_{1-x}\text{Bi}_x$ film is less than that of the InAs

spacer and the bottom region of the $\text{InAs}_{1-x}\text{Bi}_x$ film, indicating that less Bi was incorporated close to the top of the $\text{InAs}_{1-x}\text{Bi}_x$ film.

The second sample investigated by TEM had a maximum Bi incorporation of 4.5%, as determined from the (004) ω - 2θ high resolution XRD scan. In this case, the TEM sample was prepared from the droplet-forming region. The bright-field image in Fig. 5 (a) shows vertical stripe features similar to Fig. 2 (b), as well as surface droplets at the surface (example arrowed in Fig. 5 (b)). No apparent atomic ordering was visible, although horizontal growth defects were sometime observed - see the example in Fig. 5 (b).

The lattice-fringe image of a representative surface droplet, which is about 100 nm in length and 40 nm in maximum height is shown in Fig. 6 (a). Twinning and V-shaped surface grooves ((111) surface faceting) were observed in the droplet. Fast-Fourier-transform analysis was performed from regions of the matrix (Fig. 6 (b)) and the droplet (Fig. 6 (c)), respectively, in order to obtain measurements of the local lattice parameter and the angles between lattice planes. Judging from the length ratio and the angle between diffraction vectors in the diffractogram, the surface droplet has adopted a zincblende structure, with a lattice constant between those of InAs and InBi (extrapolated or calculated) [19, 20] with an $\sim 80^\circ$ tilt away from the matrix, suggesting an unidentified phase containing indium, arsenic and bismuth.

3.2 Bi-mediated $\text{InAs}/\text{InAs}_{1-x}\text{Sb}_x$ type-II superlattices

The low-magnification bright-field images of the whole $\text{InAs}/\text{InAs}_{0.81}\text{Sb}_{0.19}$ superlattice stack, such as the examples shown in Fig. 7 where the bottom half and top half of the T2SL were captured, indicated no extended structural defects over wide lateral distances. The averaged intensity line profile of the higher magnification bright-field image shown in Fig. 8 (a) was extracted in order to study the interface abruptness and the effect of the Bi surfactant. The valleys shown in Fig. 8 (b) correspond to InAs layers while the peaks correspond to the InAsSb

layers. The gradual intensity drop at the interface of InAs-on-InAsSb compared to the interface of InAsSb-on-InAs indicated interfacial broadening, as observed previously for samples grown without any surfactant [13]. Thus, it appears that use of the Bi surfactant during growth did not significantly improve the asymmetrical interfacial abruptness.

4. Conclusions

Bright-field and diffraction contrast imaging has revealed that lateral compositional modulation on the scale of several tens of nanometers exists in both the smooth and hazy regions of the $\text{InAs}_{1-x}\text{Bi}_x$ alloy films. However, no atomic ordering was observed in selected area electron diffraction patterns. The surface droplets seem to assume a tilted zincblende structure in the hazy regions, with a lattice constant between those of InAs and InBi, which is possibly a phase of $\text{InAs}_{1-x}\text{Bi}_x$. As evident from the averaged line intensity profile of bright-field image of the Bi-mediated InAs/InAs_{0.81}Sb_{0.19} type-II superlattices, the InAs-on-InAsSb interface appears to be broadened compared with the InAsSb-on-InAs interface.

Acknowledgments

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References

- [1] K. Oe, H. Asai, IEICE Trans. Electron, **E79C**, 1751 (1996).
- [2] H. Okamoto, K. Oe, Jpn., J. Appl. Phys., **37**, 1608 (1998).
- [3] S. Tixier, M. Adamcyk, T. Tiedje, Appl. Phys. Lett., **82**, 2245 (2003).
- [4] S. Francoeur, M.-J. Seong, A. Mascarenhas, S. Tixier, M. Adamcyk, T. Tiedje, Appl. Phys. Lett. **82**, 3874 (2003).
- [5] A.G. Norman, R. France, A.J. Ptak, J. Vac. Sci. Technol. B **29**, 03C121 (2011).
- [6] M. Wu, E. Luna, J. Puustinen, M. Guina, A. Trampert, Appl. Phys. Lett. **105**, 041602 (2014).
- [7] G. Vardar, S.W. Paleg, M.V. Warren, M. Kang, R.S. Goldman, Appl. Phys. Lett. **102**, 042106 (2013).
- [8] S.P. Svensson, H. Hier, W.L. Sarney, D. Donetsky, D. Wang, G. Belenky, J. Vac. Sci. Technol. B **30**, 02B109 (2012).
- [9] L. Dominguez, D.F. Reyes, F. Bastiman, D.L. Sales, R.D. Richards, D. Mendes, J.P.R. David, D. Gonzalez, Appl. Phys. Express **6**, 112601 (2013).
- [10] P.T. Webster, N.A. Riordan, C. Gogineni, S. Liu, J. Lu, X.-H. Zhao, D.J. Smith, Y.-H. Zhang, S.R. Johnson, J. Vac. Sci. Technol. B **32**, 02C120 (2014).
- [11] D.L. Smith, C. Mailhot, J. Appl. Phys. **62**, 2545 (1987).
- [12] E.H. Steenberg, B.C. Connelly, G.D. Metcalfe, H. Shen, M. Wraback, D. Lubyshev, Y. Qiu, J.M. Fastenau, A.W.K. Liu, S. Elhamri, O.O. Cellek, Y.-H. Zhang, Appl. Phys. Lett. **99**, 251110 (2011).
- [13] L. Ouyang, E.H. Sttenbergen, Y.-H. Zhang, K. Nunna, D.L. Huffaker, D.J. Smith, J. Vac. Sci. Technol. B **30**, 02B106 (2012).
- [14] K. Mahalingam, E.H. Steenberg, G.J. Brown, Y.-H. Zhang, Appl. Phys. Lett. **103**, 061908 (2013).

- [15] S.R. Johnson, Yu.G. Sadofyev, D. Ding, Y. Cao, S. A. Chaparro, K. Franzreb, Y.-H. Zhang, J. Vac. Sci. Technol. B **22**, 1436 (2004).
- [16] C. Wang, S. Tobin, T. Parodos, J. Zhao, Y. Chang, S. Sivananthan, D.J. Smith, J. Vac. Sci. Technol. A **24**, 995 (2006).
- [17] M.J. Hytch, E. Snoeck, R. Kilaas, Ultramicroscopy, **74**, 131 (1998).
- [18] Digital Micrograph script developed by C. Koch (Ulm).
- [19] K.Y. Ma, Z.M. Fang, R.M. Cohen, G.B. Stringfellow, J. Appl. Phys. **68**, 4586 (1990).
- [20] A. Janotti, S.-H. Wei, S.B. Zhang, Phys. Rev. B **65**, 115203 (2002).

Figure Captions

Fig. 1 Schematic illustration of samples studied: (a) $\text{InAs}_{1-x}\text{Bi}_x$ alloys and (b) Bi-mediated $\text{InAs}/\text{InAs}_{1-x}\text{Sb}_x$ T2SLs.

Fig. 2 (a) Bright-field TEM image of $\text{InAs}_{0.942}\text{Bi}_{0.058}$ alloy sample and the corresponding selected-area electron diffraction pattern (inset); (b) diffraction contrast image showing vertical stripe features, indicating lateral compositional modulation.

Fig. 3 (a) High-resolution image of $\text{InAs}_{0.942}\text{Bi}_{0.058}$ sample showing region close to the GaSb buffer, (b) corresponding out-of-plane strain map, and (c) average strain line profile.

Fig. 4 (a) High-resolution image of $\text{InAs}_{0.942}\text{Bi}_{0.058}$ sample showing region close to the top InAs capping layer, (b) corresponding out-of-plane strain map, (c) average strain line profile, and (d) the average out-of-plane strain line profile obtained from further GPA analysis of Fig. 3 (a) using InAs as the reference.

Fig. 5 (a) Bright-field TEM image of $\text{InAs}_{0.955}\text{Bi}_{0.045}$ sample, and (b) diffraction contrast image showed vertical stripe features, indicating lateral compositional modulation. Horizontal growth defects also visible.

Fig. 6 (a) High-resolution image showing surface droplet on the $\text{InAs}_{0.955}\text{Bi}_{0.045}$ film. Fast Fourier transform from square region of interest chosen in (b) InAs capping layer, (c) droplet region, and (d) combination of both diffractograms.

Fig. 7 (a) Bright-field images of Bi-mediated $\text{InAs}/\text{InAs}_{0.81}\text{Sb}_{0.19}$ T2SL showing: (a) bottom half, and (b) top half, also indicating no extended defects over large lateral distances.

Fig. 8 (a) Bright-field TEM image showing upper part of $\text{InAs}/\text{InAs}_{0.81}\text{Sb}_{0.19}$ T2SL, and (b) the averaged line intensity profile from region indicated in (a).

(a)

(b)

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8